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THE EVALUATION OF AIR CATHODES FOR POTENTIAL
USE IN DEVELOPMENT OF ALUMINUM-AIR CELLS

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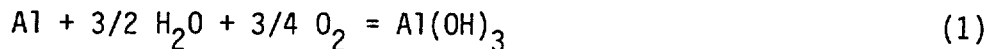
ABSTRACT

Four air cathodes representing the products of three manufacturers were tested under conditions of continuous and intermittent polarization in order to determine their suitability for testing large-scale aluminum-air single cells. Polarization tests on 25 cm^2 samples were conducted at 60°C in flowing electrolyte ($6 \text{ M NaOH} + 1.4 \text{ M Al(OH)}_3 + 0.06 \text{ M Na}_2\text{Sn(OH)}_6$), over the current density range, $0 - 8 \text{ kA/m}^2$. Continuous polarization tests were conducted under these conditions at 1.3 kA/m^2 for up to 312 hours. Intermittent tests consisted of alternate periods of (1) polarization at 1.3 kA/m^2 for 1 hour under the above conditions and (2) standby at open circuit in cold, stationary, super-saturated caustic-aluminate solutions for up to 24 h. The W electrode performed for 312 h with a decrease of potential of 0.11V at 1.3 kA/m^2 .

The X standard electrode failed to sustain continuous polarization for longer than 12 h. Both W and Z electrodes met or nearly met polarization requirements in the Request for Proposal No. 6352009. The tests demonstrated that the W electrode is sufficiently durable and low in polarization to be used for testing 0.1 m^2 aluminum-air cells.

INTRODUCTION

An aluminum-air battery is currently under development as a mechanically-refuelable power source for electric vehicles. In this concept, the battery operates as a fuel cell and is charged by the addition of aluminum anode plates (at intervals of 1600 - 3200 km) and tap water (at intervals of 400 km). The net cell discharge reaction is as follows:



The oxygen for reaction (1) is supplied by air flowing over the catalytic surface of an air cathode. The reaction product is transformed within the battery system into a semi-dry, alkali-free powder of trihydrated alumina (hydrargillite polymorph). In this form, the product is periodically withdrawn from the vehicle (at intervals of 400 - 600 km) for reprocessing into new anode plates at industrial sites.^{1,2,3}

The power cell system design is shown in Figure 1. Caustic-aluminate electrolyte is circulated (1 liter) between the galvanic cell stack and an electrolyte storage tank. Part of this electrolyte stream is passed through the crystallizer containing hydrargillite seed particles and operating as a fluidized bed (flow-through rate, ca. 0.25 liters/s). Electrolyte temperature during cell operation is maintained at 60°C (+5°) through a combination of passive and active heat transfer and evaporative-cooling. During standby periods, the electrolyte drains into the thermally-insulated storage tank, and crystallization of Al(OH)₃ continues under nearly adiabatic conditions.

During vehicle operation, heavier seed particles are preferentially removed from the crystallizer, washed counter-current to a flow of distilled water, drained under a back pressure of 7 - 15 kPa, and transferred to a storage tank.

The tap-water circulation subsystem serves four functions: (1) trace dirt and CO₂ removal from the incoming air stream; (2) saturation of air-stream with water vapor at 60° C.; (3) heat transfer from electrolyte to air stream; and (4) active heat rejection to the environment. Domains of operating conditions for the battery have been defined from computer

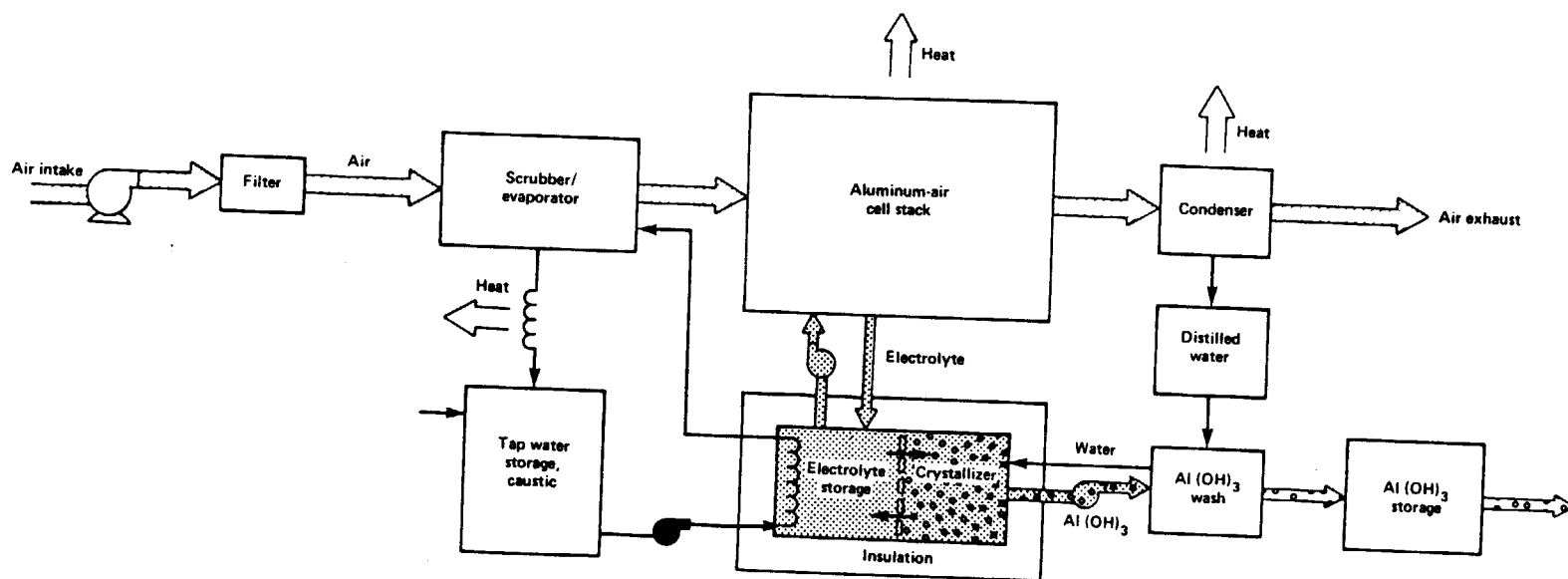


Figure 1: Flow diagram of Aluminum-air power cell system. Tap water is introduced into the electrolyte by evaporation into the incoming airstream in an evaporator tank held in thermal contact with the electrolyte storage tank.

simulation of internal heat and mass transfers,⁴ and the crystallizer has been designed on the basis of industrial and laboratory kinetic data for the decomposition step of the Bayer Process.⁵

Critical technical challenges of the program are: (1) the development of a cost-effective air cathode for use in the battery electrolyte for the duty cycles encountered in vehicular applications; (2) mechanical means for rapid addition of 30 - 60 anode plates to the cell hardware, and provisions for full utilization of the anode (i.e., without excessive anode parasitic corrosion or unconsumed residuals); (3) the production of an anode alloy of high electrochemical efficiency at high rates of dissolution, using calcined battery product as a feedstock for a single-step reduction process; and (4) the development of reliable processes and components for the crystallization of industrially useful hydrargillite on-board the vehicle.

An "Invitation for Proposal" (IFP) has been issued for the development and procurement of air-cathodes for use in cell hardware development and testing.⁶ As part of this IFP, interested air-cathode developers were encouraged to supply samples (25cm^2 - active area) to be tested at Lawrence Livermore Laboratory in aluminum-air cell or half-cell configurations. Tests were conducted under the operating conditions (temperature, hydrodynamics, composition, current density) anticipated for automotive applications. These conditions are given in Table I.

Polarization and life requirements were specified in the IFP as follows. The steady-state air cathode potential should be positive to the line $V_c = -0.05 - 0.4i$ where V_c is the air cathode polarization ($V_c = V_{\text{cathode}} - V_{\text{reference}}$), the reference electrode being the Hg/HgO electrode in 6 M NaOH, and "i" being the current density in A/cm^2 . The cathode should maintain this performance after a minimum of 200 hours of continuous operation.

Three cathode manufacturers supplied samples for testing. The first manufacturer supplied cathode W, the second manufacturer supplied cathode X, and the third manufacturer supplied cathodes Y and Z. This report describes the results of the tests.

TABLE I
ANTICIPATED OPERATING CONDITIONS OF AN ALUMINUM-AIR
ELECTRIC VEHICLE POWER CELL

Electrolyte Composition

Sodium hydroxide (as NaOH)	4-8M; 6M most probable
Sodium aluminate (as $\text{Al}(\text{OH})_3$)	1.5-3.2M, variable
Minor components	
Ga	0.2 g/liter
Sodium stannate	0.03-0.1M

Operating Temperature (Isothermal)

50-70°C

Standby Electrolyte Temperature
(Quasi-adiabatic)

varies; determined by heat generation by precipitation, heat of mechanical agitation; and slow heat loss by conduction through insulated walls of electrolyte storage tank

Electrolyte Flow Conditions

Reynolds Number*

500-2500

Air Flow Rate and Conditions

Multiple of stoichiometric oxygen consumption rate**

4-10

Air pressure differential between air and electrolyte

7kPa (1 psi), air positive

Galvanic Cell Operating Conditions

Anode current density:
sustained

0.08 to 0.2 A/cm^2

peak (transient)

0.5 A/cm^2

time-average

0.13 A/cm^2

Time-average aluminum dissolution rate

0.727 g/s at 0.13A/cm²

Cell Configuration

Anode (or cathode) projected surface area per cell (2 anodes per cell)

2000 cm^2

Number of cells per battery

30

Length of electrodes in direction of flow

25 cm

Width of electrodes

40 cm

Electrode separation

0.15 to 0.35 cm

Orientation of electrolyte flow

vertical

* $\text{Re} = 2sv/u$, where s = electrode separation; v = linear flow rate; and u is kinematic viscosity.

**Oxygen is consumed at a rate of 0.89 g/g-Al for a stoichiometric factor of 1

EXPERIMENTAL

Materials

The W electrodes supplied consist of a hydrophobic layer, a Pt-catalyzed carbon PTFE layer, and a silver-plated nickel screen which is the current collector. The developer indicated that the platinum in these electrodes may be depleted by oxidative-dissolution in the caustic electrolyte under open-circuit conditions.

The X air electrode consists of a laminated structure based on a metallic grid made of nickel plated steel which acts both as a current collector and as a support for the catalyst. The catalyst is a supported carbon structure mixed with a wet proofing agent to stabilize the electrolyte/catalyst/air interface. An outer layer of gas permeable hydrophobic material, such as PTFE, bonded to the catalyzed grid prevents leakage of electrolyte through the cathode. The cathode was supplied with a teflon backing layer which was removed for these experiments.

Air cathode Y is a planar fabric of overall dimension 3 1/2 X 3 1/2 inches with an active surface area of 50 - 60 cm². It is supplied with a proprietary current collector. The platinum loading is 0.33 ± 0.03 mg/cm². Air cathode Z is supported on a metallic grid rather than fabric and has a platinum loading of 0.4 ± 0.04 mg/cm².

The reagent grade sodium hydroxide used in the electrolyte preparation was supplied by Mallinckrodt. The 6 M NaOH + 1.5 M Al(OH)₃ solutions were prepared by first dissolving a weighed amount of NaOH in the appropriate volume of distilled water, then adding a weighed amount of 99.999% aluminum metal (supplied by Cominco American) and slowly dissolving the aluminum by heating and stirring. After dissolution the solution volume was adjusted by adding distilled water. The stock 1 M sodium stannate solutions were also prepared by dissolving a weighed amount in a known volume of distilled water. The reagent grade Na₂Sn(OH)₆ used was supplied by Baker and Adamson, General Chemical Division.

A schematic diagram of the apparatus used in these tests is shown in Figure 2. A comparison of Figure 1 with Figure 2 indicates that the laboratory apparatus in Figure 2 reproduces the air cathode environment in the power cell as shown in Figure 1. The air stream, shown on the left of the figure is dried, the CO_2 removed by the soda lime, and then rehumidified at a temperature of $52\text{--}55^\circ\text{C}$ which will give approximately the same vapor pressure as the sodium hydroxide solutions at 60°C . The air is then passed over the air cathode from top to bottom and finally passed through a column of water which creates a back pressure of 3 - 6kPa (12-25 inches of water). This back pressure helps to prevent the electrolyte from seeping through flaws in the air-cathode. The electrolyte is pumped from the heated reservoir through a flow meter and then into the cell. Knife blade immersion heaters were used (100 - 250 W), with power supplied by a variable AC powerstat. It was possible to maintain the temperature of the liquids in the humidifier and electrolyte storage vessels to better than $\pm 1^\circ\text{C}$ by careful monitoring and adjustment of the powerstat.

The reference electrode (Hg/HgO , 6M NaOH) is inserted in the electrolyte storage tank, and thereby is maintained at the same temperature as the cell. The use of a Luggin capillary was avoided because of the difficulty of insuring reliability over the extended periods of unmonitored polarization. Results of polarization were corrected for electrolyte IR drop, using a value estimated from solution conductivity and geometric considerations (see 'Comparison of Results and Conclusions').

Figure 3 shows an exploded diagram of the experimental cell. Anode and cathode surfaces lie in a vertical plane. Air enters an air plenum at the top of the cell and flows downward over the cathode surface. Electrolyte flows vertically and upward. Four experimental systems were constructed to allow simultaneous testing.

Silicone rubber sealant was used to prevent air leakage between the Lucite block and current collector. Stopcock grease was used on the other surfaces to minimize the leakage of electrolyte.

When testing air cathodes, the experimental unit was operated as an oxygen-air cell, with oxygen being evolved at a nickel or stainless steel anode.

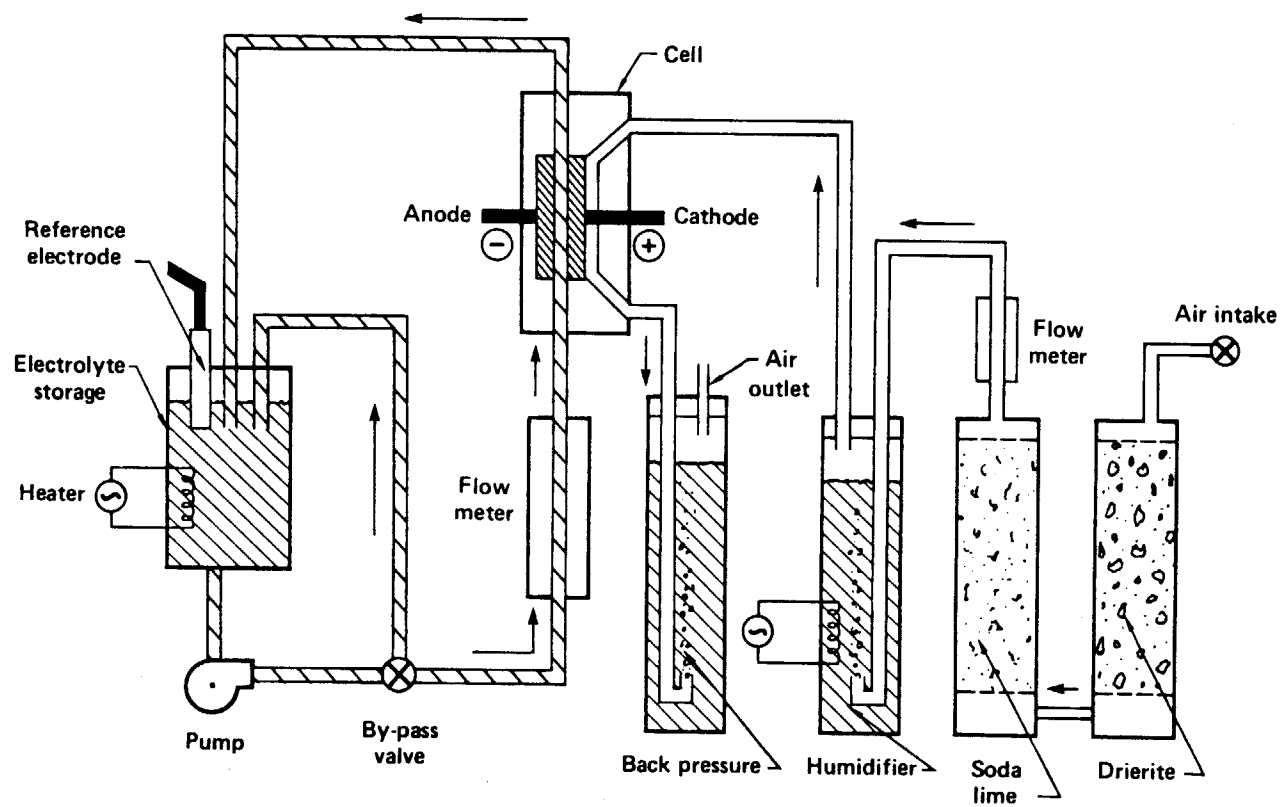


Figure 2: Experimental system for air-cathode testing. Constant current was supplied by an external power source.

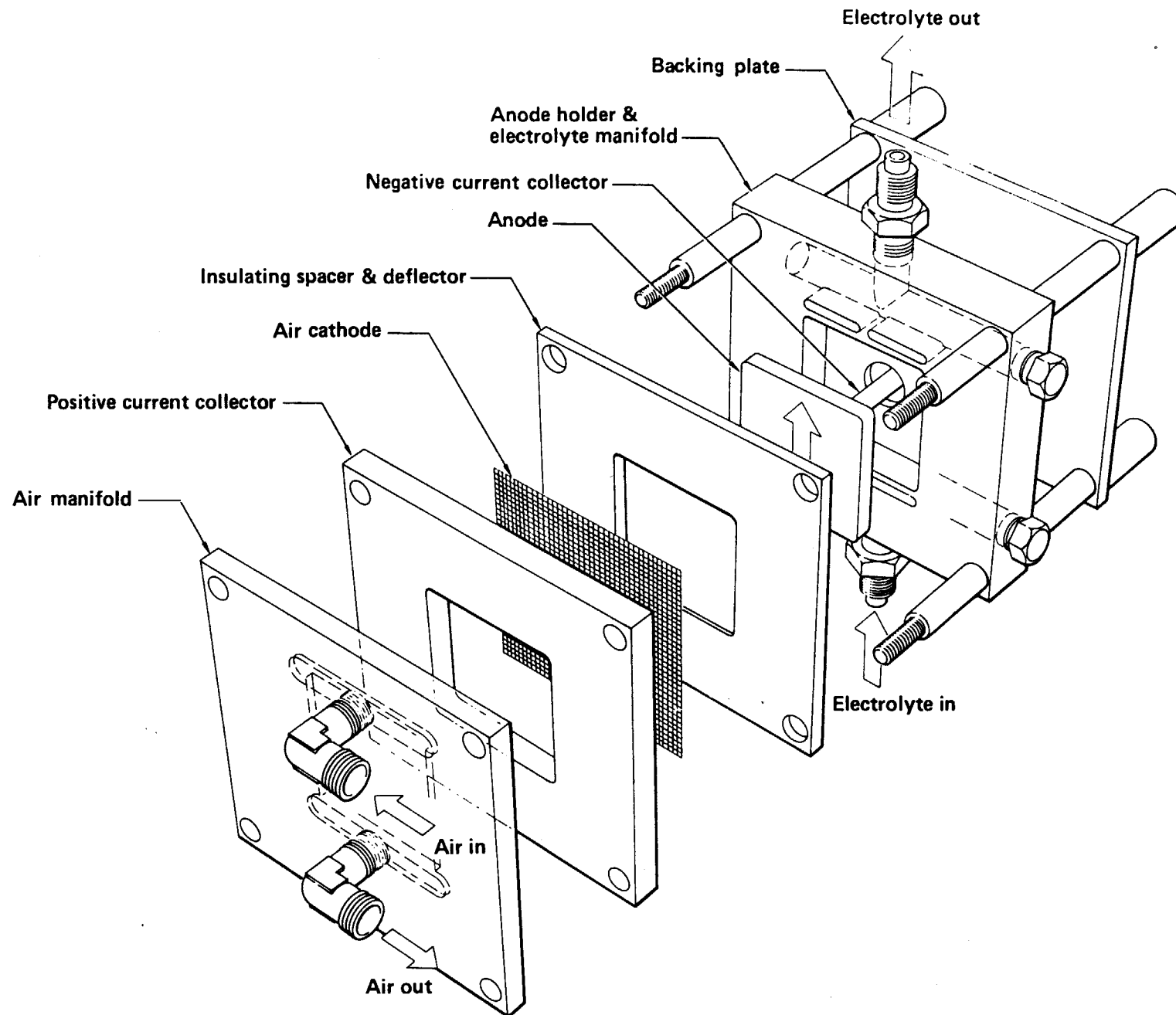


Figure 3: Experimental cell for testing air cathodes.

The voltage difference between the air cathode and the Hg/HgO reference electrode was recorded with a Gould Brush 110 strip chart recorder. Periodically, polarization curves were obtained using a Hewlett-Packard Model 70454 X-Y Recorder. The constant-current power supplies for each cell were designed and built at the Lawrence Livermore Laboratory.

Test electrolyte solutions were prepared from stock solutions (6M NaOH + 1.5 M $\text{Al}(\text{OH})_3$) by additions of aliquots of 1 M $\text{Na}_2\text{Sn}(\text{OH})_6$. These solutions were then adjusted by additions of solid NaOH to the final compositions 6M NaOH + 1.4M $\text{Al}(\text{OH})_3$ + 0.06M $\text{Na}_2\text{Sn}(\text{OH})_6$.

Electrodes from each supplier were subjected to two kinds of experiments: (1) continuous polarization (at 1.3 kA/m^2 , with periodic polarization scans from 0 - 10 kA/m^2 for periods of up to 312 hours; and (2) short periods of polarization (at 1.3 kA/m^2 , or with scans) alternating with longer intervals on standby (with cold electrolyte retained in the cell).

To compensate for water losses by evaporation, distilled water was periodically added to the reservoirs. Determination of electrolyte composition before and after experimental runs indicated no more than a 3% change (aluminate concentrations were determined by conductivity measurements; NaOH was determined by acid titrations; and tin concentrations by x-ray fluorescence).

The experimental parameters common to these tests are: electrolyte temperature - $60 \pm 1^\circ\text{C}$, air flow rate - $800 \text{ cm}^3/\text{min}$, electrolyte flow rate - 0.6 gal/min (0.038 l/sec or $\text{Re} = 900$), a constant current density of 0.130 A/cm^2 , and electrode area of 25 cm^2 .

In the initial experiments with the Z fabric air cathode, it was discovered that the electrolyte pressure was greater than the air pressure. According to the specifications in Table 1, the air should be positive by 7kPa (53mm Hg). We therefore attached a mercury manometer to cell Number 3 to measure the pressure difference. We found that the electrolyte pressure was positive to air by as great as 46mm Hg (26 in of water). By changing the electrolyte flow system (eliminating valves on the downstream side and discharging the cell electrolyte directly into the reservoir), decreasing the electrolyte flow rate to 0.20 gal/min, and adding more back pressure on the air stream (from 12 to 25 in of water), we were able to operate the cell with the air pressure ca. 2kPa greater than the electrolyte pressure. The Z screen electrode tests were conducted under these modified conditions.

INDIVIDUAL TEST RESULTS

W Air Cathode

The W air cathode exceeded the 200-hour specification for the continuous polarization test with very little decrease in potential at constant current density. These results were obtained with pressure on the electrolyte side of the cathode greater than that on the air side. The results and pertinent experimental parameters are given in Table II. The polarization loss after the 312-hour test was 0.11V. The test was terminated after 312 hours without catastrophic cathode failure.

Figure 4 shows polarization curves of the W cathode during the first hour, after 216 hours and after 312 hours of continuous operation. (The initial curve is obtained from the intermittent test of a similar air cathode.). The curves are shown as measured and include the IR drop through the electrolyte: approximately 0.41 V at 1 A/cm^2 .

The alternate polarization and standby tests consist of one hour of polarization at 0.13 A/cm^2 at a temperature of 60°C , followed by four hours of standby at open circuit in cold, supersaturated electrolyte. The one-hour operation is repeated and the cell is similarly shut down until the next morning. A fresh electrode was used for these tests.

The voltage as a function time at a constant current density of 0.13 A/cm^2 is shown in Figure 5. As is seen, after some initial oscillations, the voltage settles to -0.2 volts versus the Hg/HgO reference electrode. The current versus voltage plots for cycle #1 and cycle #9 are shown in Figure 6. The curves are reproducible at low-current densities but not at higher current densities. Note that the ninth-cycle curve shows lower polarization at high current densities than does the 1st cycle curve.

X Air Cathode

The standard X air cathodes were used in these tests after removing the Teflon layer. The pertinent data from the two tests are given in Table III. The loss of performance of the X standard air cathode was undoubtedly due to flooding of the electrode. In the initial test, we observed that the electrolyte had penetrated the electrode in a number of places and was vigorously attacking the current collector on the air side.

Table II

Results of the Continuous Polarization and Alternate
Polarization/Standby Tests of the W Air Cathodes

Air Cathode	Initial Polarization vs. Hg/HgO ($i=0.13 \text{ A/cm}^2$)	Final Polarization vs. Hg/HgO ($i=0.13 \text{ A/cm}^2$)	Test Duration (Hours)	Electrolyte Composition
26AB 185E 3435-3 (Apr. 1979) (Continuous Polarization Test)	-0.18	-0.29V	312	NaOH: $6.3 \pm 0.1 \text{ M}$ Al(OH)_3 : $1.40 \pm 0.1 \text{ M}$ $\text{Na}_2\text{Sn(OH)}_6$: 0.06 M
26AB 188-50E 3435-5 (Apr. 1979) (Alternate Polarization and Stand-by Test)	-0.18	-0.2V	102	NaOH: 6.0 M Al(OH)_3 : 1.6 M $\text{Na}_2\text{Sn(OH)}_6$: 0.06 M

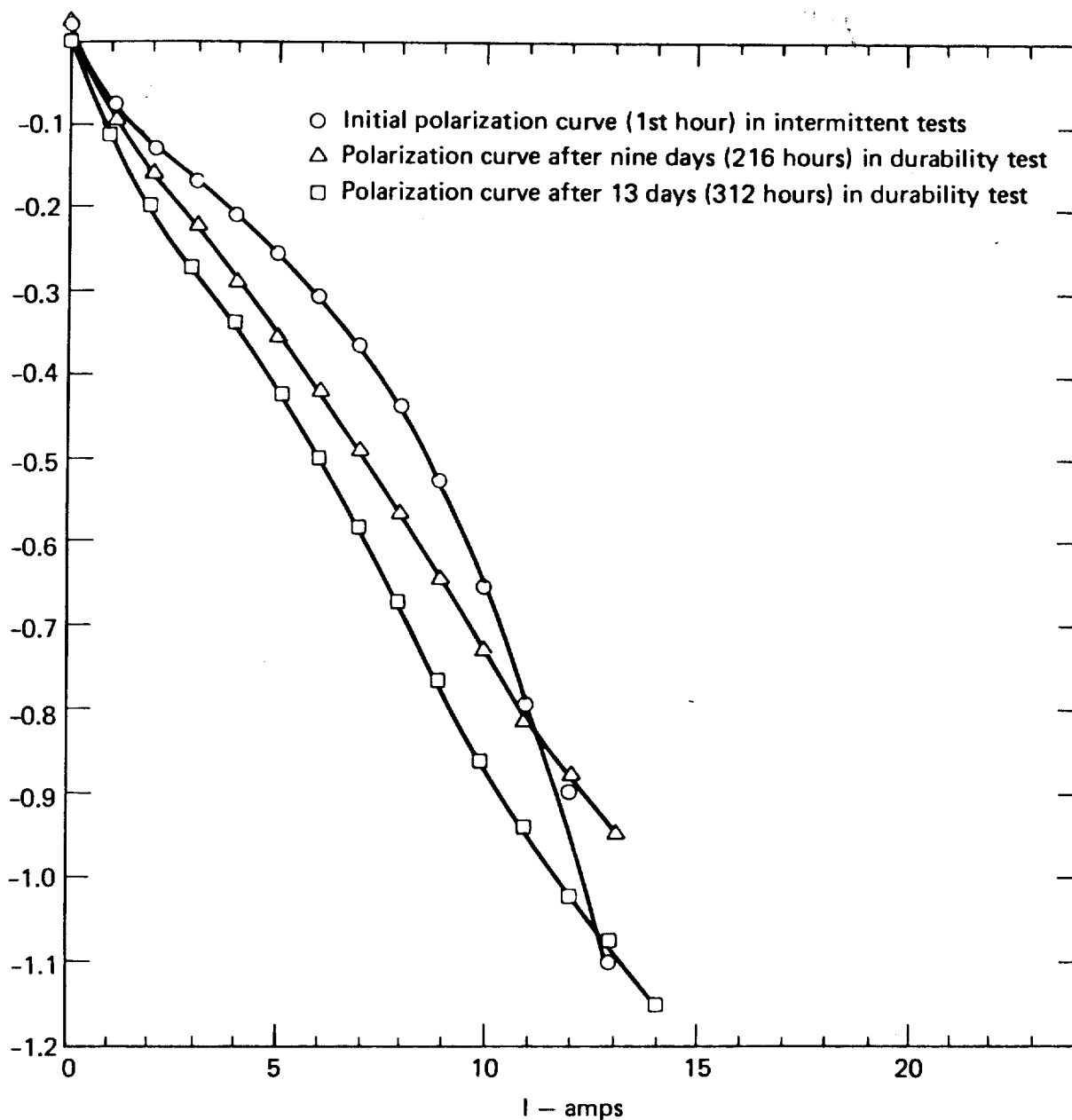


Figure 4: Polarization curves for the W Air Cathode (Continuous Polarization Test) Electrolyte: 6.3M NaOH, 1.4M Al(OH)₃, 0.06M Na₂Sn(OH)₆; Temp: 60°C; Electrolyte flow rate: 0.04 l/s; Air flow rate: 0.013 l/s.

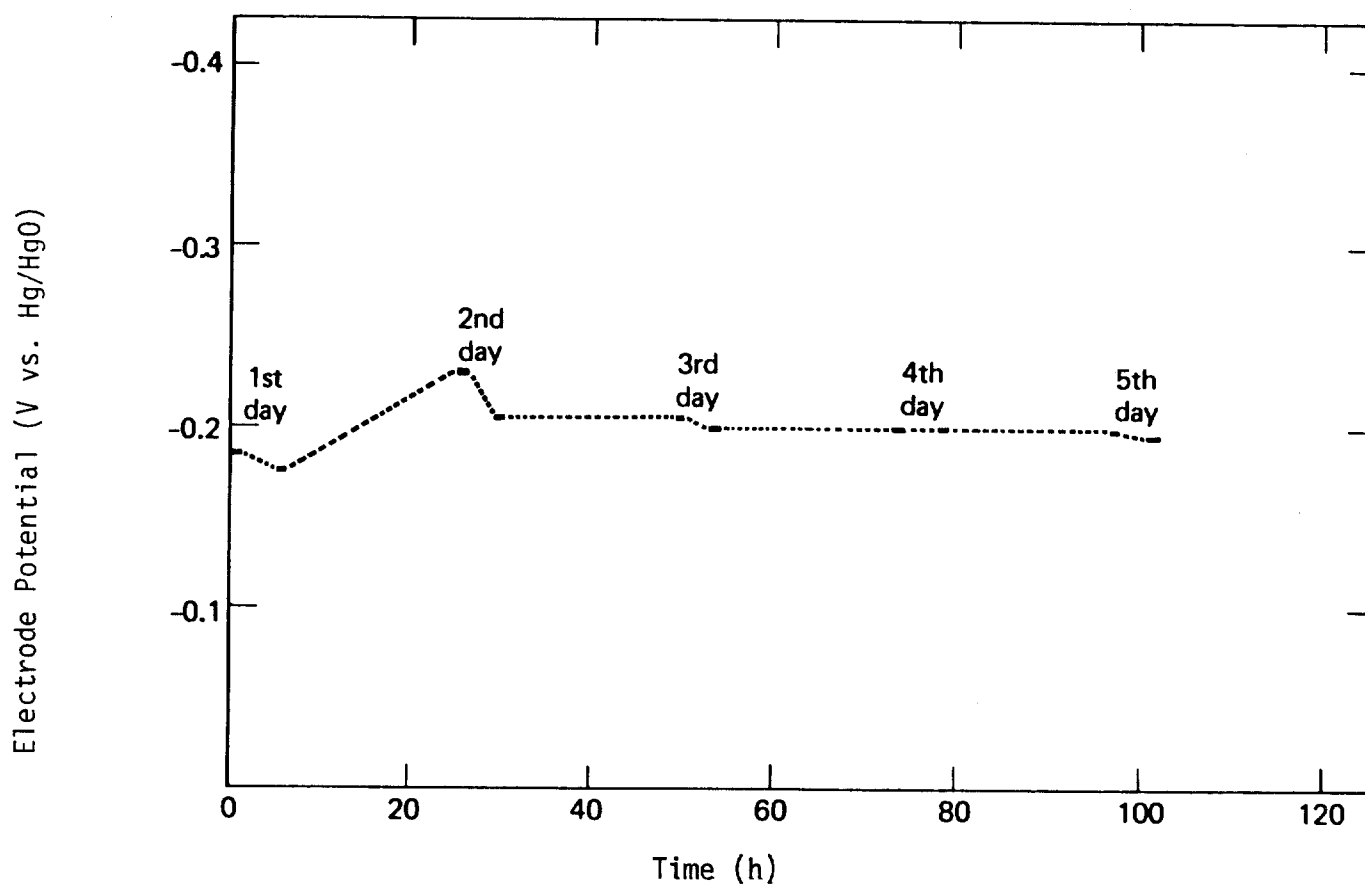


Figure 5: Plot of V_c vs. Time at $i = 0.13 \text{ amp/cm}^2$ - W Air Cathode
(Alternate polarization and stand by tests). Electrolyte: 6.3M NaOH,
1.4M $\text{Al}(\text{OH})_3$, 0.06M $\text{Na}_2\text{Sn}(\text{OH})_6$; Temp: 60°C ; Electrolyte flow
rate: 0.04 l/s; air flow rate: 0.013 l/s.

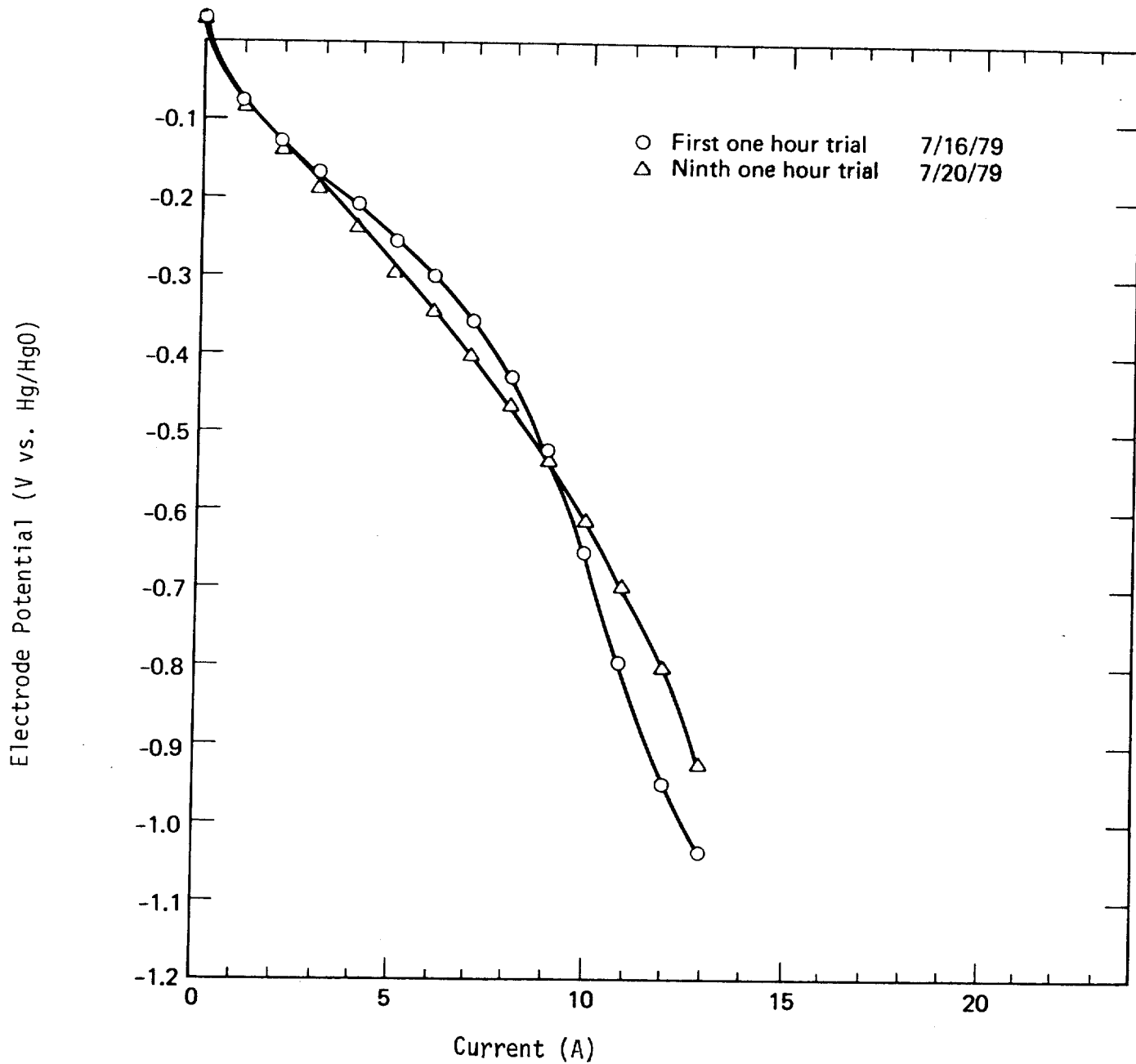


Figure 6: Air cathode polarization curves - W Air Cathode (Alternate polarization and standby tests). Electrolyte: 6.0M NaOH, 1.6 M $\text{Al}(\text{OH})_3$, 0.06M $\text{Na}_2\text{Sn}(\text{OH})_6$; Temp: 60°C, Electrolyte flow rate: 0.013 l/s.

Table III

Results of the Continuous Polarization and Alternate
Polarization/Standby Tests of the X Air Cathodes

Air Cathodes	Test Duration	Initial	Final
		Polarization vs. Hg/Hg0 ($i=0.13 \text{ A/cm}^2$)	Polarization vs. Hg/Hg0 ($i=0.13 \text{ A/cm}^2$)
X Standard (As received - minus Teflon)	(After 9 hours)	-0.2	-0.75V
	(After 19 hours)		fluctuated randomly
X Standard (sintered)	(After 21 hours)	-0.33	-2.0V

Electrolyte composition:

NaOH: 6.0 M,

Al(OH)₃: 1.4 M

Na₂Sn(OH)₆: 0.06 M

The second manufacturer suggested that flooding could be minimized by sintering the electrode. This is done by removing the Teflon and asbestos layers of the cathode and heating it for twenty minutes at 310°C in a muffle furnace. We prepared the second electrode sample by this procedure. As seen in Table III, the electrode performance was no better. The excess electrolyte pressure undoubtedly enhanced the flooding, causing the electrode failure. Figure 7 shows the polarization curve we obtained after the second hour of the second test.

Prototech

The data from the four tests of Z electrodes are given in Table IV. The first continuous polarization test of the fabric electrode was unsuccessful due to flooding of the air cathode, which probably was enhanced by the excess electrolyte pressure.

The third manufacturer suggested two ways to improve the performance of the Z air cathode: (1) insure that the pressure on the air side of the cathode is 3 inches of water (5.6mm Hg) greater than the electrolyte pressure and (2) polarize the air cathode in nitrogen (or pure oxygen) during the early stages of the test. The nitrogen pre-treatment gives hydrogen evolution at the cathode at $V_c = -0.8$ V versus Hg/HgO. This nitrogen pre-treatment was tried first, but as shown in Table IV did not improve the performance. We next set up a manometer and measured the air-electrolyte pressure difference across the cathode. As noted earlier, the electrolyte pressure was 46 mm Hg greater than the air pressure. Our apparatus was modified so that the air pressure would be at least 6 mm greater than the electrolyte pressure. The continuous polarization test of the RA 24 Screen-Type air cathode was performed with this revised set-up. Note that to insure that the air pressure was greater than the electrolyte pressure, the electrolyte flow rate was reduced to 0.35 g/min, which gave an air stream overpressure (relative to the electrolyte) of 13mm Hg.

Figure 8 shows the electrode potential versus Hg/HgO as a function of time during the continuous polarization test. Figure 9 illustrates the time history of the continuous polarization test of this electrode.

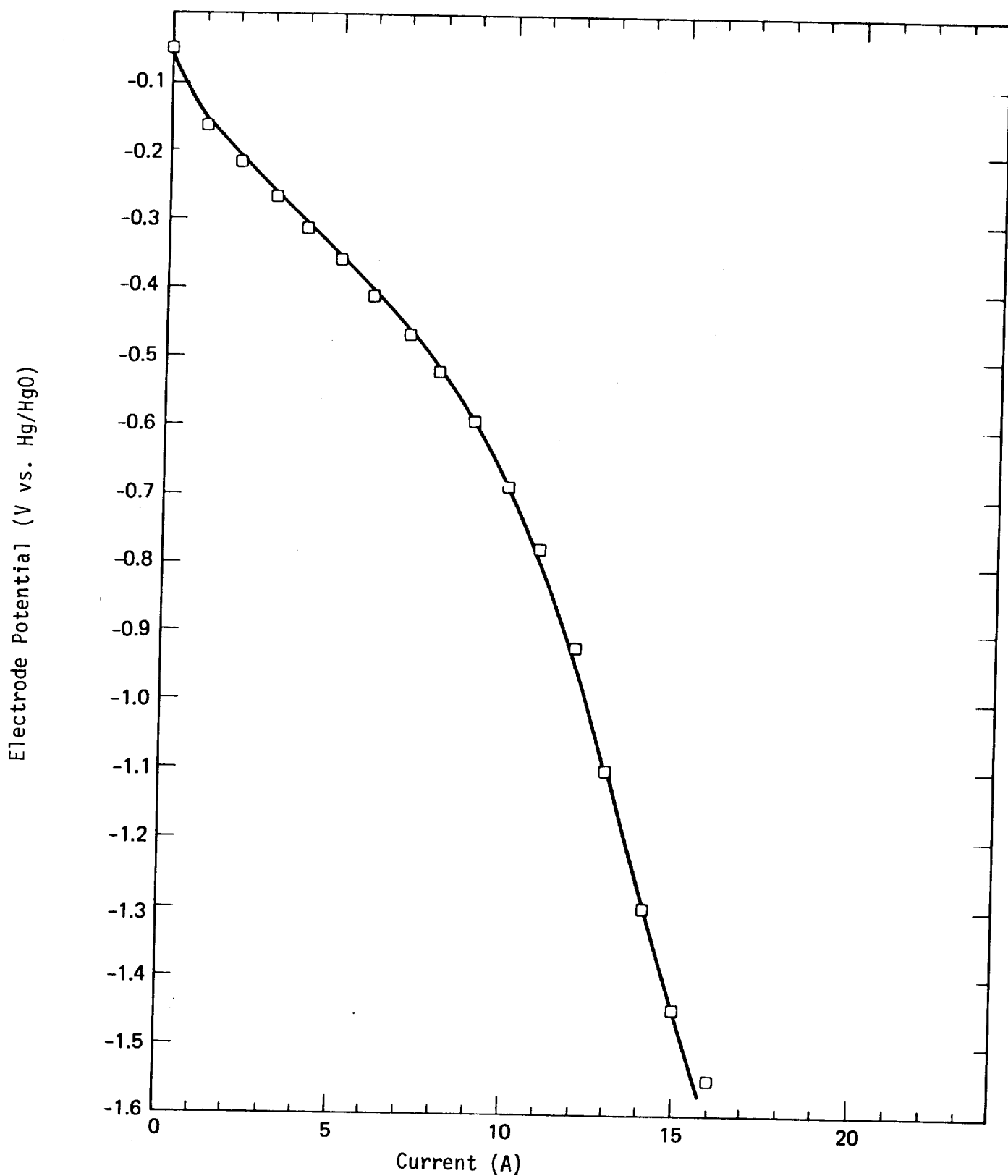


Figure 7: Polarization curve for the X air cathode (continuous polarization test). Electrolyte: 6.0 M NaOH, 1.4 M $\text{Al}(\text{OH})_3$, 0.06 M $\text{Na}_2\text{Sn}(\text{OH})_6$; Temp: 60°C ; Electrolyte flow rate: 0.04 l/s, air flow rate: 0.013 l/s.

Table IV

Results of the Continuous Polarization and Alternate Polarization/Standby Tests of the Y and Z Air Cathodes

Air Cathode	Initial Polarization vs. Hg/HgO ($i=0.13 \text{ A/cm}^2$)	Final Polarization vs. Hg/HgO ($i=0.13 \text{ A/cm}^2$)	Test Duration (Hours)	Electrolyte Composition
Y - RA19-100-cc-121 (Fabric - dated 3/27/79 - Continuous Polarization)	-0.25V	-0.42V(9 hours)	18	NaOH: 6.0 M Al(OH) ₃ : 1.4 M Na ₂ Sn(OH) ₆ : 0.06 M
Y - RA-100-cc-12.3 (Fabric Continuous Polarization-Nitrogen Pretreatment)	-0.28V	-2.0V	17	Same
Z - RA24 Screen (Continuous Polarization)	-0.17V	-0.57V	142	Same
RA24 Screen (Alternate Polarization & Standby-fresh Electrode)	-0.2V	-0.2V	162	Same

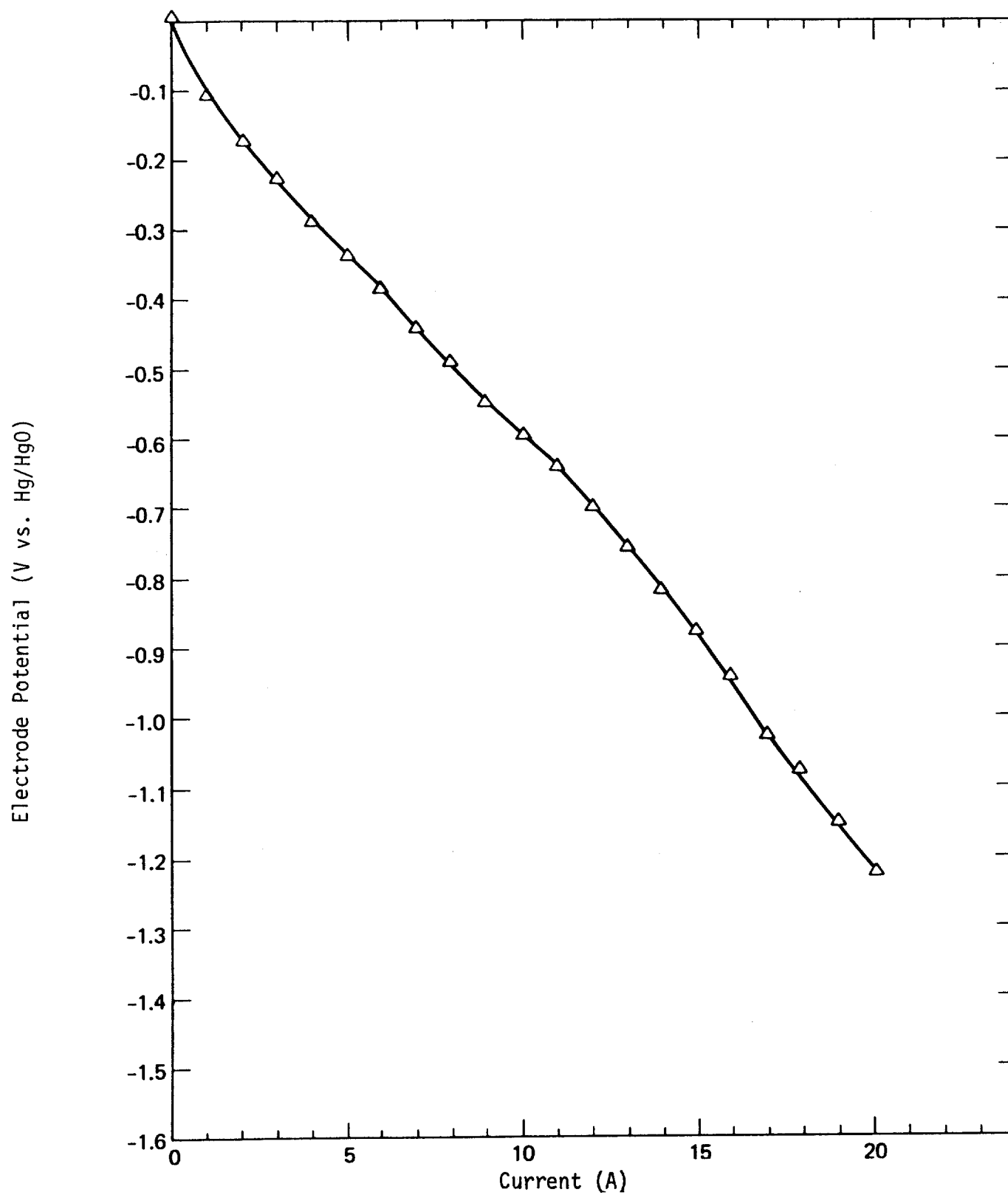


Figure 8: Polarization curve of the Y fabric air cathode (continuous polarization test). Electrolyte: 6.0 M NaOH, 1.4 M $\text{Al}(\text{OH})_3$, 0.06 M $\text{Na}_2\text{Sn}(\text{OH})_6$, Temp: 60°C, Electrolyte flow rate: 0.04 l/s; Air flow rate 0.013 l/s.

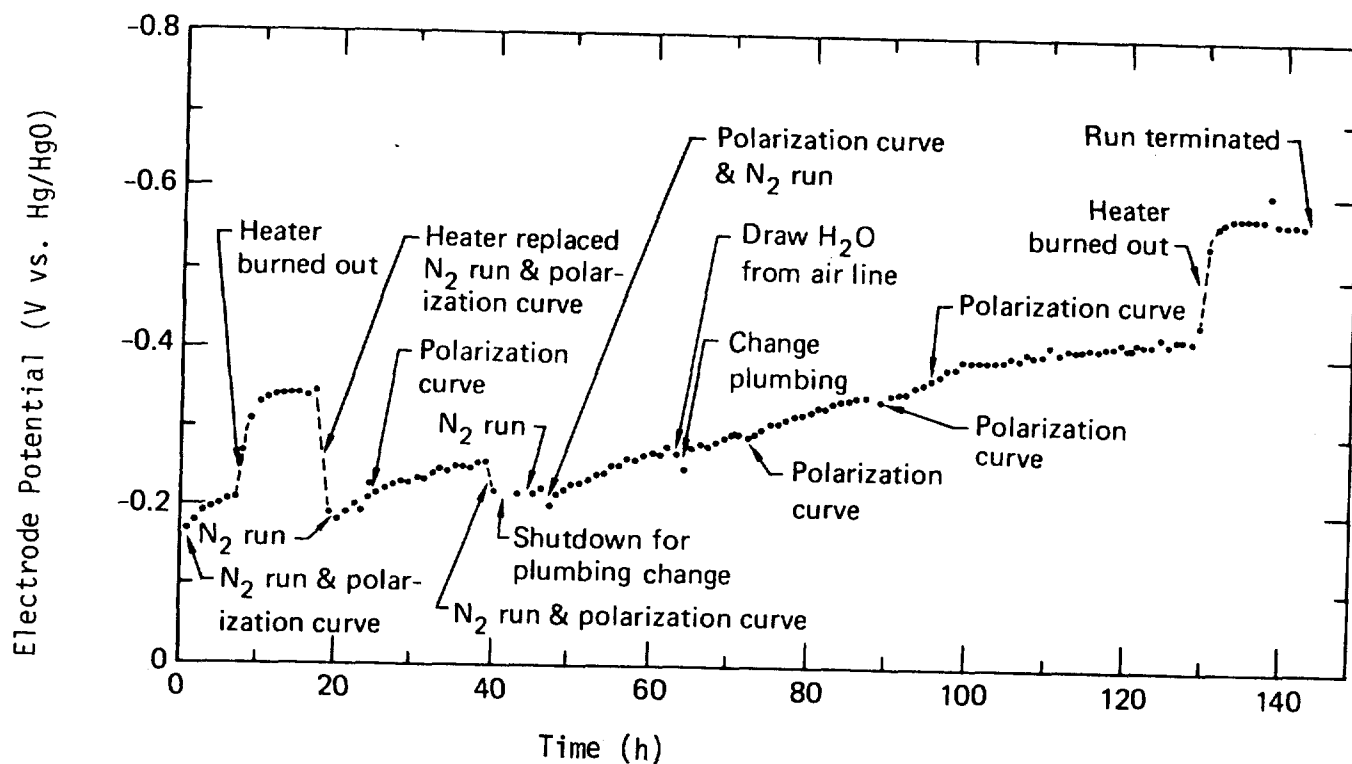


Figure 9: Time History of the Z Screen air cathode (continuous polarization test) ($i = 0.13 \text{ A/cm}^2$). Electrolyte: 6.0 M NaOH, 1.4 M $\text{Al}(\text{OH})_3$, 0.06 M $\text{Na}_2\text{Sn}(\text{OH})_6$, Temp: 60°C , Electrolyte flow rate: 0.023 l/s, Air flow rate: 0.013 l/s.

The test was terminated when a heater failed, causing the cathode potential to decrease to -0.57V . Figure 10 also illustrates the deterioration of air cathode potential versus time.

The time history of the RA 24 Screen Type cathode potential in the alternate polarization and standby tests is given in Figure 11 and summarized in Table IV. During the last one-hour run at 162 hours total, the electrode potential deteriorated by more than 0.1V . Figure 12 shows three of the polarization curves obtained in this test.

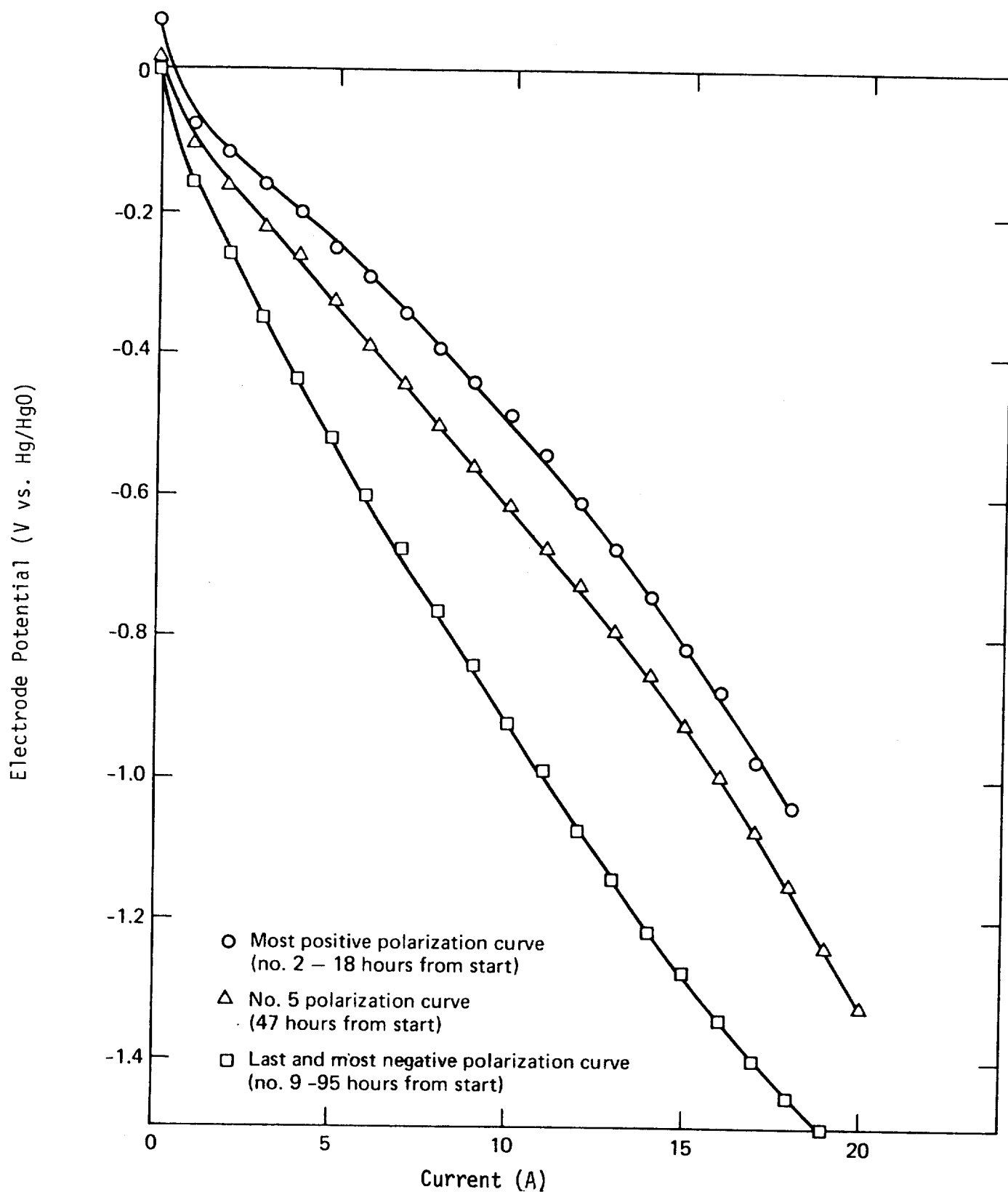


Figure 10: Air cathode polarization curve. Z electrode (continuous polarization test). Electrolyte: 6.0 M NaOH, 1.4 M $\text{Al}(\text{OH})_3$, 0.06 M $\text{Na}_2\text{Sn}(\text{OH})_6$; Temp: 60°C , Electrolyte flow rate: 0.023 l/s, air flow rate: 0.013 l/s.

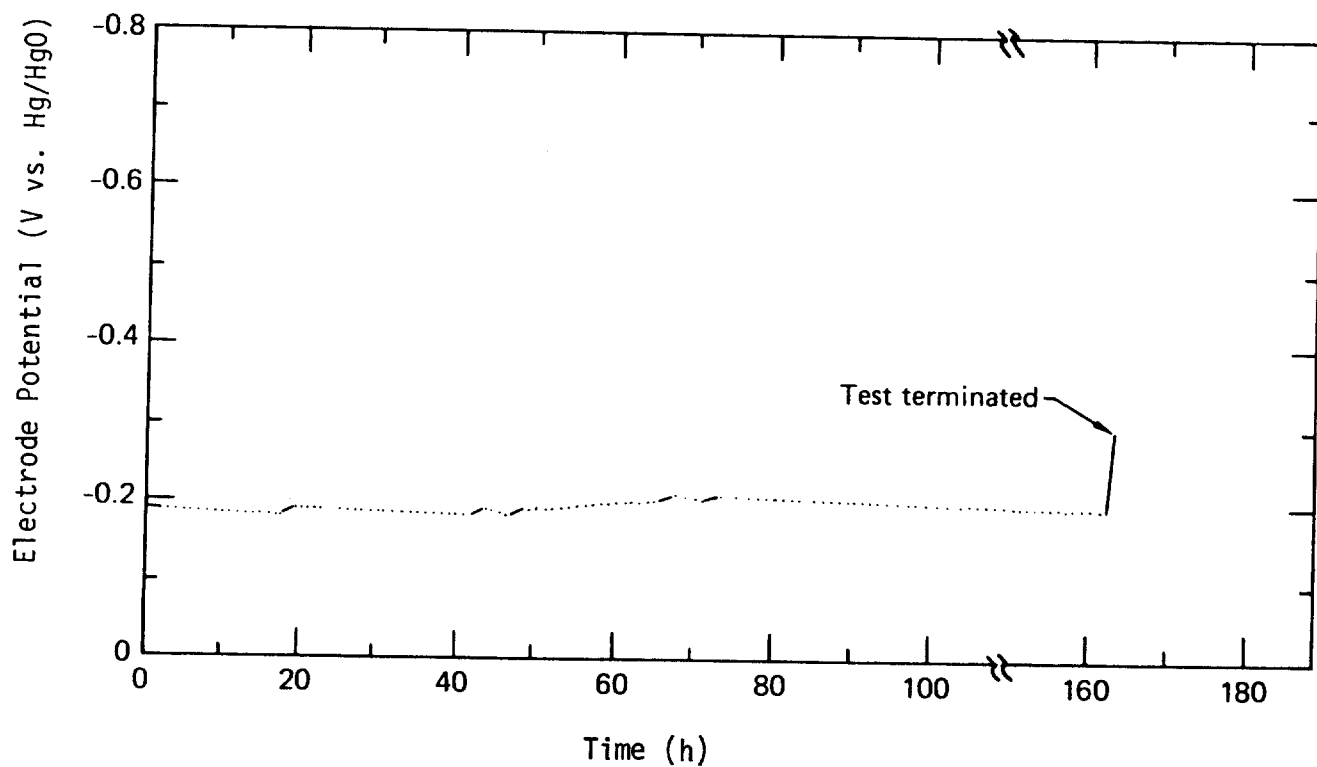


Figure 11: Time history of the Z air cathode (alternate polarization and standby test)($i=0.13 \text{ A/cm}^2$). Electrolyte: 6.0 M NaOH, 1.4 M Al(OH)_3 , 0.06 M $\text{Na}_2\text{Sn(OH)}_6$; Temp: 60°C , Electrolyte flow rate: 0.023 l/s, Air flow rate: 0.013 l/s.

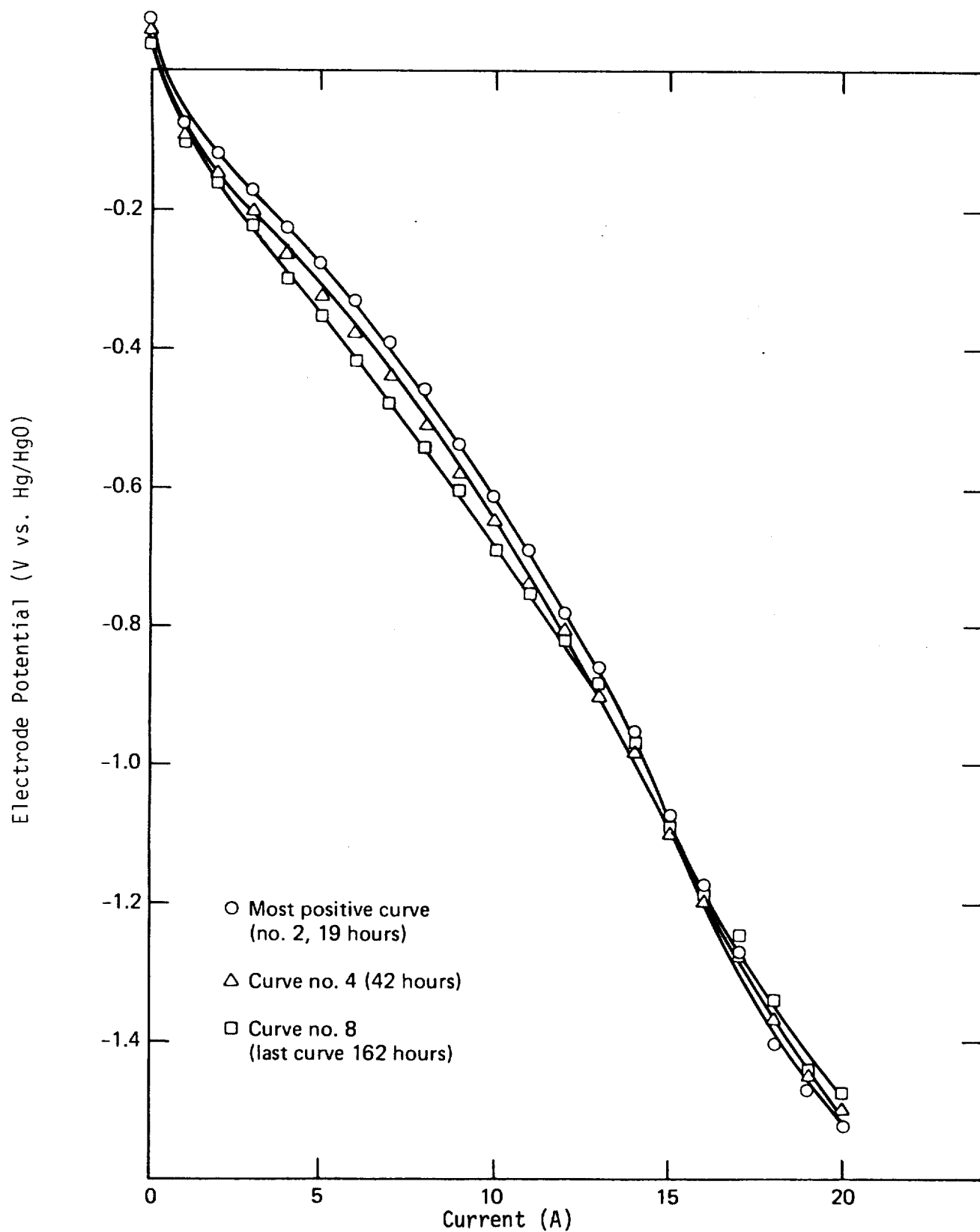


Figure 12: Polarization Curves, Z screen air cathode (alternate polarization and standby test). Electrolyte: 6.0 M NaOH, 1.4 M $\text{Al}(\text{OH})_3$, 0.06 M $\text{Na}_2\text{Sn}(\text{OH})_6$; Temp: 60°C , Electrolyte flow rate: 0.023 l/s, Air flow rate: 0.013 l/s.

COMPARISON OF RESULTS AND CONCLUSIONS

Estimation of Electrolyte Ohmic Potential Drop

All of the polarization curves presented thus far have included an ohmic potential (IR) drop caused by the electrical resistance of the electrolyte. In order to compare the measured air cathode polarization curves to the ideal curve specified in the work statement of the IFP (see Introduction), it is necessary to subtract this potential drop from the cathode polarization curves. Our method of estimating this contribution to the electrode potential is developed below.

Figure 13 shows a schematic diagram of the cross-section of the electrolytic cell used in this work. The distance a is the electrode separation which is equal to 0.32 cm. The distance $b = 0.23$ cm is from an imaginary line at the center point of the electrolyte channel opening to the air cathode and represents the distance we use to compute the IR drop from the reference electrode (which is effectively at an infinite distance) to the air cathode.

The value of the measured voltage of the air cathode, $V_c(\text{meas.})$, versus the Hg/HgO reference electrode in terms of the actual voltage, $V_c(\text{actual})$ and the IR drop is given by

$$V_c (\text{meas.}) = V_c (\text{actual}) - \frac{ib}{K} \quad (2)$$

where the latter term is the IR drop, i is the current density, and K is the electrical conductivity of the electrolyte. A value of $K = 0.57 \text{ ohm}^{-1}\text{cm}^{-1}$ was taken from the conductivity versus concentration plots in Reference 7. Substitution of these values of b and K into equation (2) and rearranging gives:

$$V_c(\text{actual}) = V_c(\text{measured}) + 0.41i \quad (3)$$

Figure 14 compares the electrolyte IR drop with the air cathode polarization curves. It is apparent that the IR drop is a large fraction of the cathode polarization.

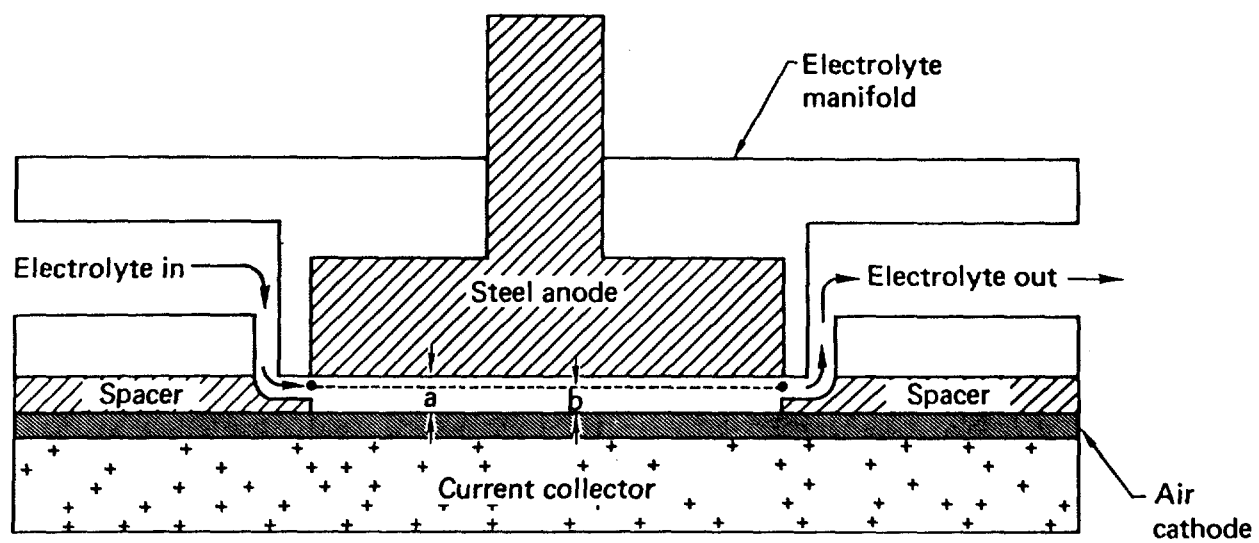


Figure 13: Cross section of the experimental cell.

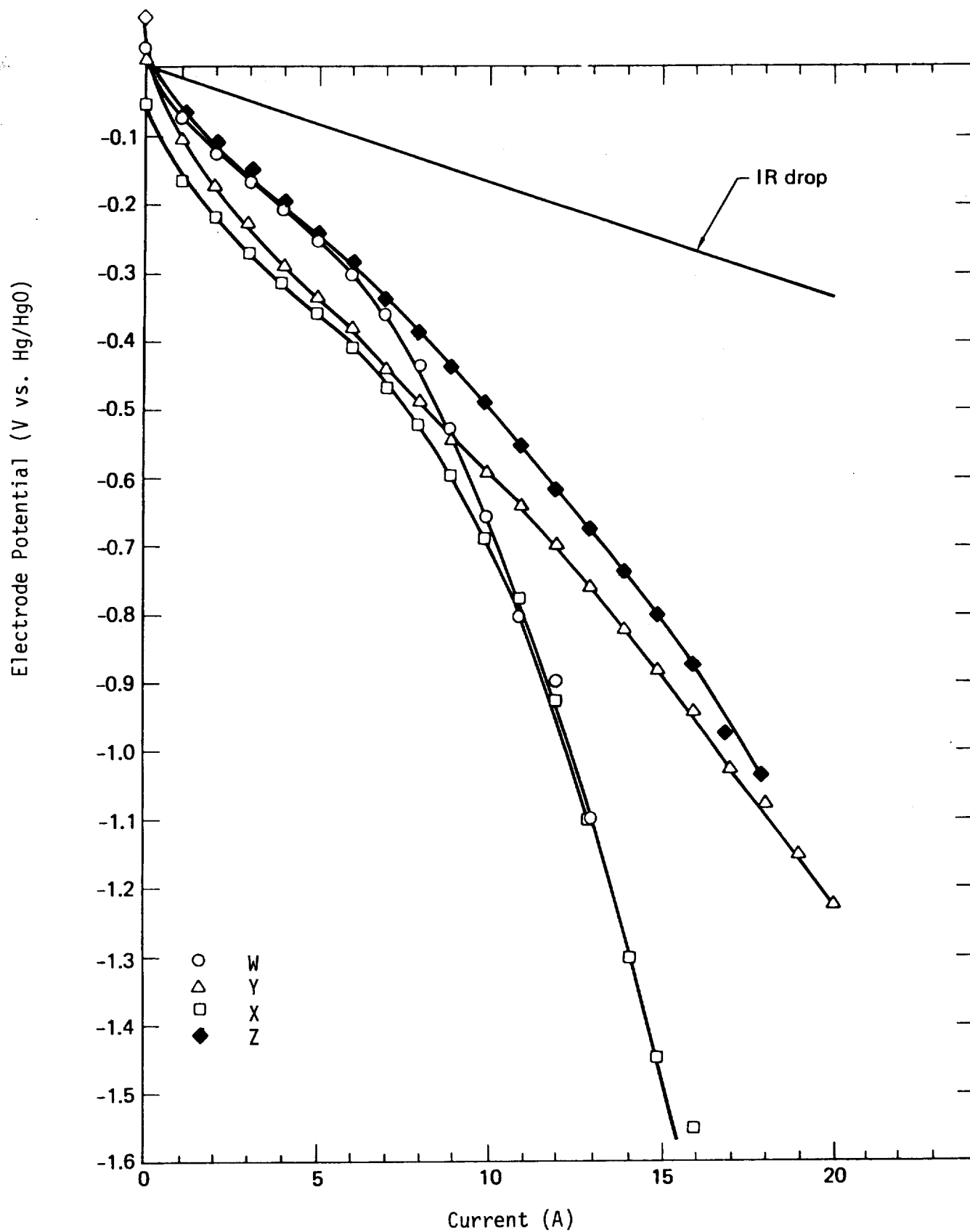


Figure 14: Comparison of the IR drop with the air cathode polarization curves.

COMPARISON OF AIR CATHODE POLARIZATION CURVES

Figure 15 compares the polarizations curves of the four electrodes tested corrected for IR drop, to that of the goal specified in the work statement of the Invitation For Proposal. The W cathode comes closer to meeting the IFP goal, especially at low current density. There is a portion of each of these s-shaped curves that is nearly linear. This portion of each curve has been fit to a straight line using the Hewlett-Packard 67 Linear Regression Method. The current density, the IR drop, and the corrected values of V_c are given in Table V. The brackets indicate the linear portions of each curve. Also indicated in Figure 11 are the linear equations for the straight line portion of each curve. These equations are:

$$W \quad V_c = -0.0378 - 0.689i \quad (4)$$

$$X \quad V_c = -0.124 - 0.776i \quad (5)$$

$$Y \quad V_c = -0.0697 - 0.905i \quad (6)$$

$$Z \quad V_c = -0.0178 - 0.761i \quad (7)$$

Another important comparison is the air cathode performance in an aluminum-air cell. This comparison is shown in Figure 16. Note that $V_a = V_{anode} - V_{reference}$. The comparison is somewhat difficult since some experimental conditions varied. The experimental conditions for each air cathode are given in Table VI. Note that each anode was different and this, of course, also had a bearing on the cell voltage. Note in this particular comparison, that the Y air cathode suffers the least polarization. Note also that the electrolyte flow rate was 0.3 gal/min. and the air flow rate was 1.6 l/min. Under these conditions, the pressure drop across the air cathode was nearly eliminated.

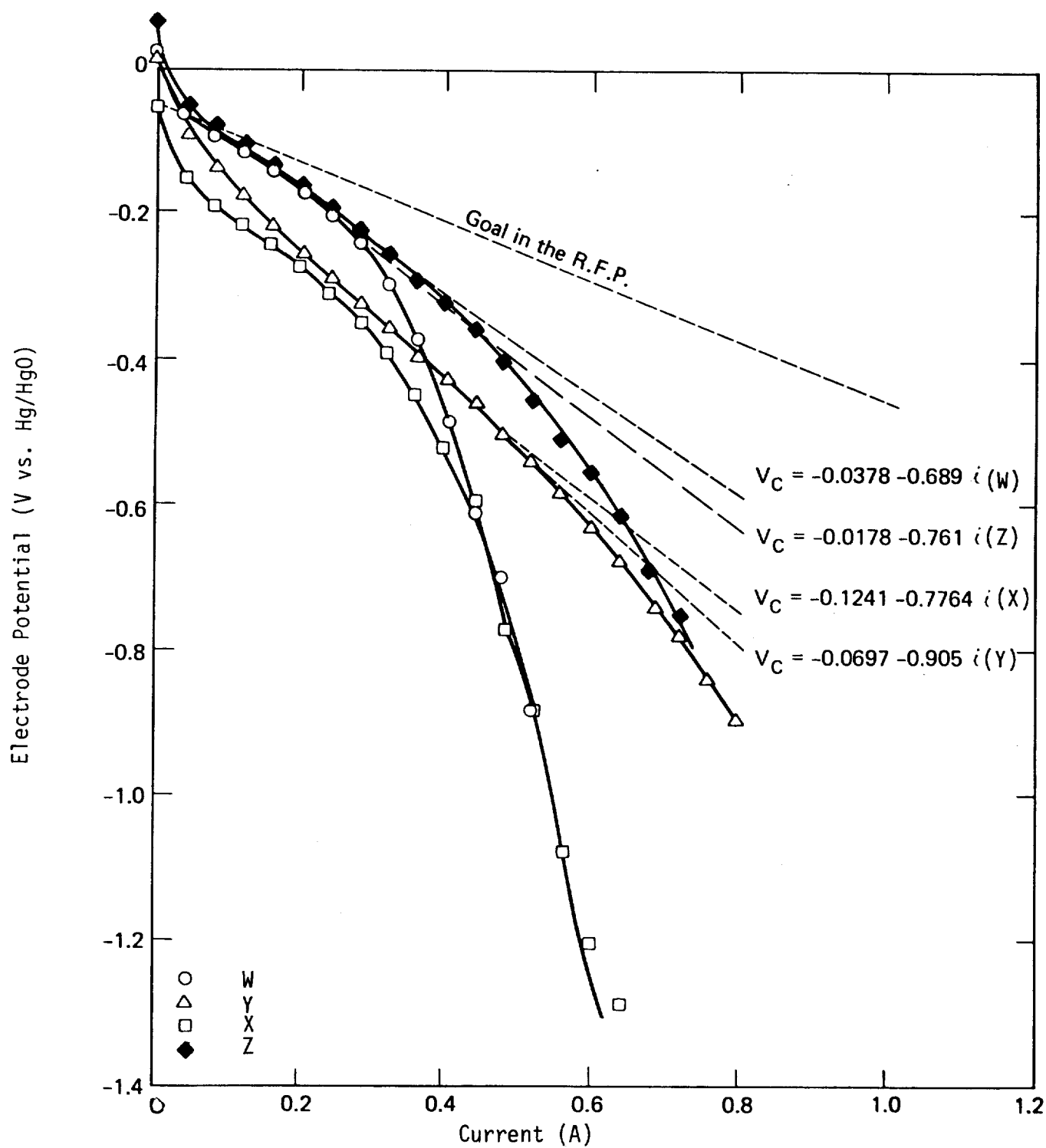


Figure 15: Comparison of the air cathode polarization curves with the curve specified in the RFP. Electrode potential has been corrected for the estimated IR drop between reference electrode and cathode.

TABLE V
Corrected values of V_c *

I – amps	i – amps/cm ²	IR Drop – volts	V_c (W)	V_c (Y) fabric	V_c (X)	V_c (Z)
0	0	0	+0.250	+0.15	-0.050	+0.075
1	0.04	0.0164	-0.064	-0.094	-0.154	-0.059
2	0.08	0.0328	-0.097	-0.142	-0.187	-0.082
3	0.12	0.0492	-0.121	-0.181	-0.221	-0.106
4	0.16	0.0656	-0.144	-0.219	-0.245	-0.134
5	0.20	0.0820	-0.173	-0.253	-0.278	-0.168
6	0.24	0.0984	-0.207	-0.292	-0.312	-0.192
7	0.28	0.1148	-0.245	-0.330	-0.350	-0.225
8	0.32	0.1312	-0.304	-0.359	-0.389	-0.259
9	0.36	0.1476	-0.377	-0.397	-0.447	-0.292
10	0.40	0.1640	-0.491	-0.431	-0.521	-0.326
11	0.44	0.1804	-0.620	-0.460	-0.600	-0.360
12	0.48	0.1968	-0.703	-0.503	-0.768	-0.403
13	0.52	0.2132	-0.887	-0.547	-0.887	-0.457
14	0.56	0.2296		-0.590	-1.070	-0.510
15	0.60	0.2460		-0.634	-1.204	-0.554
16	0.64	0.2624		-0.678	-1.288	-0.613
17	0.68	0.2788		-0.746		-0.696
18	0.72	0.2952		-0.780		-0.755
19	0.76	0.3116		-0.838		
20	0.80	0.3280		-0.897		
r^2 = Coefficient of determination for linear fit			0.9962	0.9983	0.9982	

* Volts vs. Hg/HgO; data is corrected for estimated IR drop between cathode and reference electrode.

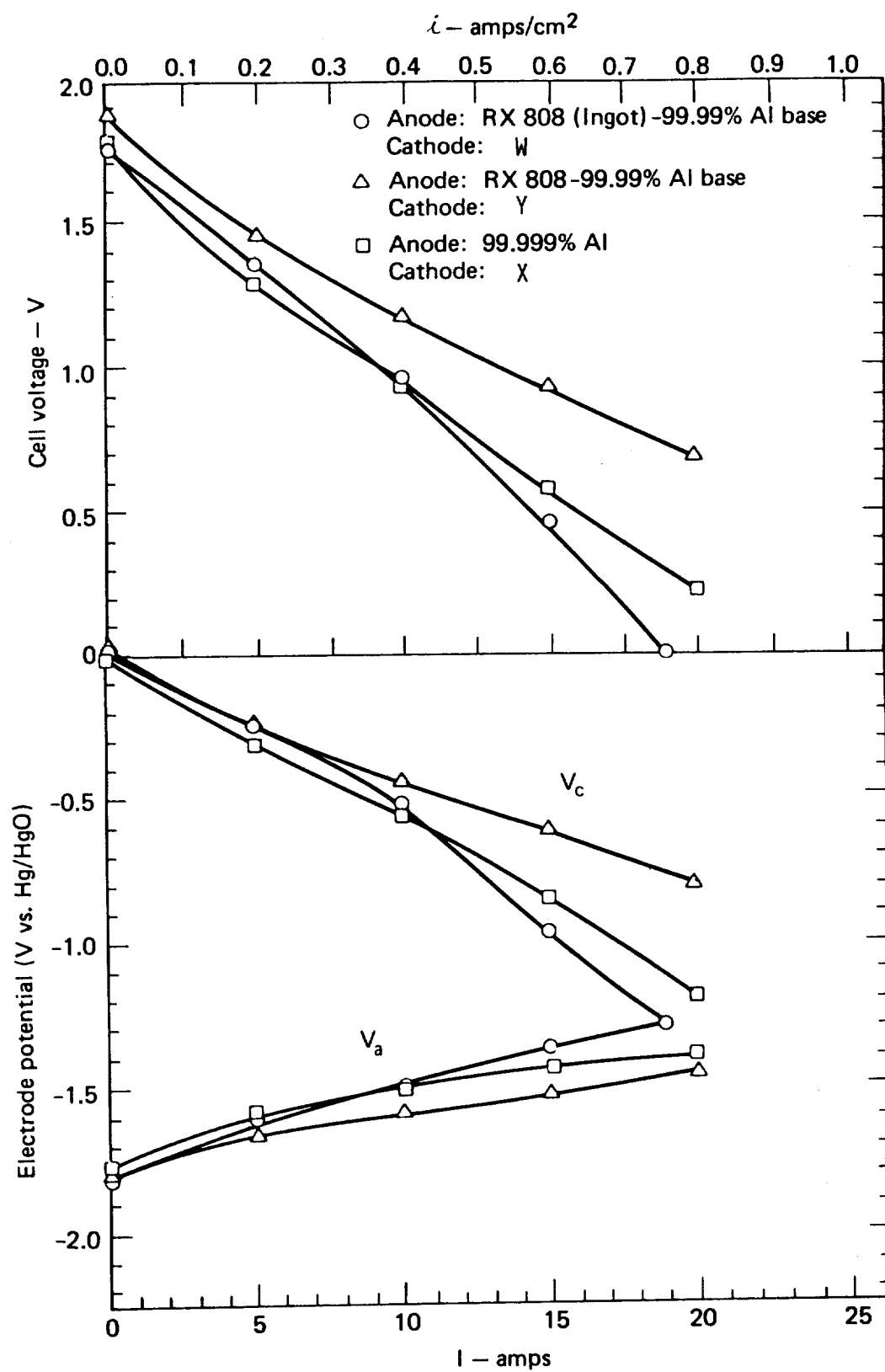


Figure 16: Comparison of aluminum air cells.

TABLE VI

EXPERIMENTAL CONDITIONS: AL-AIR SINGLE CELL PERFORMANCE

Experimental Parameter	Air Cathodes		
	W	X	Y
Anode	RX808 (INGOT) 99.99% Al Base	99.999% Al	RX808 99.99% Al Base
Electrolyte Concentrations			
NaOH	6.2 M	6.0 M	6.0 M
Al(OH) ₃	1.7 M	1.0 M	1.0 M
Na ₂ Sn(OH) ₃	0.06 M	0.06 M	0.05 M
Electrolyte Flow Rate	1 Gal/min.	1 Gal/min.	0.5 Gal/min.
Air Flow Rate	0.8 l/min.	0.8 l/min.	1.6 l/min.
Temperature	70 ± 1°C	70 ± 1°C	70 ± 1
Electrode Area	25 cm ²	25 cm ²	25 cm ²
Interelectrode Gap	0.32 cm	0.32 cm	0.32 cm

A comparison of polarization curves obtained after extended periods of polarization at 1.3 kA/m^2 is shown in Fig. 17. While the initial polarization curve of the Z electrode was most noble of the electrodes tested, the W electrode proved highly durable and maintained low polarization after 312 hours.

It should be emphasized that these tests do not establish the performance limits of the air-cathodes. Test of the electrodes conducted by the suppliers showed both excellent polarization behavior (exceeding the requirements of IFP No. 6352009⁶) and durability. Differences in results can be attributed in part to our failure to control critical parameters (pressure drop), ignorance of pretreatment procedures recommended by the suppliers, and differences between our experimental conditions and the operating conditions for which the electrodes were designed.

CONCLUSIONS

Based on laboratory tests, the W electrode is sufficient for large-scale cell testing from the standpoint of polarization behavior, durability, and mechanical structure of electrode and current collector. The Z electrodes showed excellent polarization characteristics, and can likely be modified to produce structures of sufficient durability for large-scale testing. The X electrode failed to perform for extended periods under our experimental conditions; these results were understandable, given the fact that the X electrode was designed for low current-density discharge in ambient-temperature potassium hydroxide solutions.

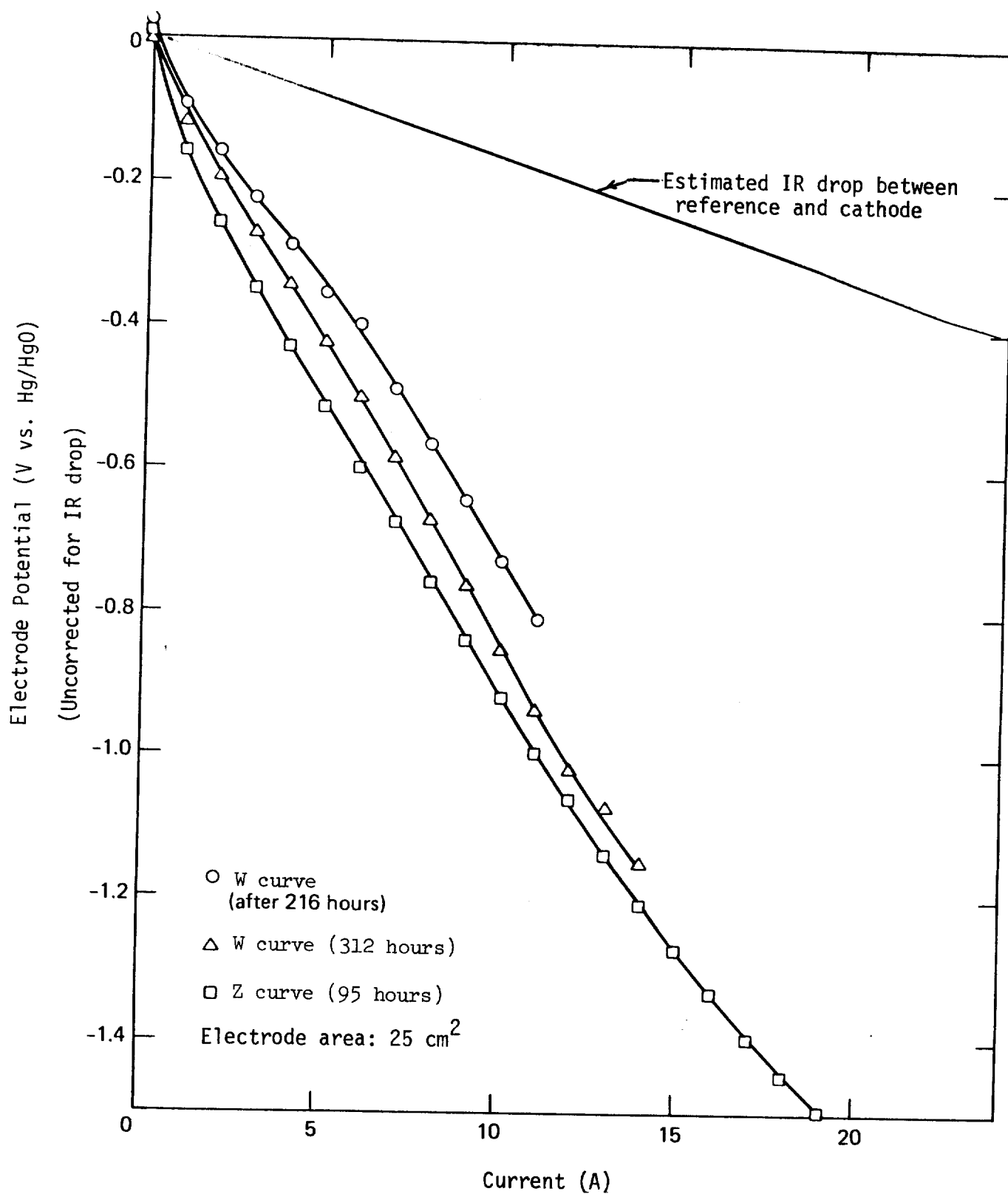


Figure 17: Comparison of the final polarization curves for Z and W air cathodes. Polarization curves were obtained after the indicated interval of continuous polarization at 0.13 A/cm².

ACKNOWLEDGEMENTS

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